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(21) International Application Number: PCT/US98/22576 (22) International Filing Date: 23 October 1998 (23.10.98) (30) Priority Data: 60/062,738 23 October 1997 (23.10.97) US (71)(72) Applicants and Inventors: VAN DER AAR, Cornelis, P., J. [NL/NL]; Golsstraat 79, NL-7553 ME Hengelo (NL). VAN OOIJ, Wim, J. [NL/US]; 154 Annandale Drive, Fairfield, OH 45014 (US). (74) Agents: PEACOCK, Bruce, E. et al.; Biebel & French, 35 East First Street, Dayton, OH 45402 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: RUBBER TO METAL BONDING BY SILANE COUPLING AGENTS		
(57) Abstract Adhesion of rubber to a variety of metals (aluminum, stainless steel, mild steel and brass) is effectively achieved by the application of an organofunctional silane (I) and a non-organofunctional silane (II) to the requisite surface. Preferably, the organofunctional silane (I) is a vinyltrialkoxysilane with the non-organofunctional silane (II) preferably comprising an alkoxylated substituted alkyl silane. The silanes (I) and (II) are at least partially hydrolyzed and are normally provided in the form of a EtOH/H ₂ O solution. Bonded joints formed by these adhesive treatments can withstand fuel degradation tests indicating that the treatments can be used, for example, to bond metal and rubber surfaces in automotive and other environments in which the joined parts will be contacted by fuels, oil and/or organic solvents.		

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RUBBER TO METAL BONDING BY SILANE COUPLING
AGENTS

Cross Reference to Related Application

5 This application claims the benefit of prior filed copending U.S.
Provisional Application No. 60/062,738 filed October 23, 1997.

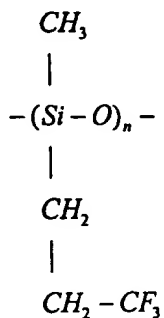
Field of the Invention

10 This invention relates to methods for adhering rubber to metal
surfaces.

Background of the Invention

Reliable metal to rubber adhesion is required for many commercial
and industrial parts. For example, rubber to metal adhesion is required in the
15 automotive, medical, appliance and other industries where basic functions such as
fluid control, energy conversion, sealing, vibration isolation and/or combinations of
these functions are required. Additionally, tire to metal, metallic reinforcement of
conveyor belts and hoses, and vibration dampening on motor and railroad mounts are
further examples of industrial situations in which a variety of metals need to be
20 adhesively bound to an associated rubber substrate.

Fluorosilicone elastomers have become increasingly popular due to
their excellent high and low temperature performance. These elastomers also
demonstrate advantageous resistance to fuels, oils, chemicals etc. due to the presence
of the trifluoropropyl moiety in their repeat unit formula



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The polysiloxanes are crosslinked via pendent vinyl moieties by curing with peroxides. Compounds of fluorosilicones are formulated with reinforcing silica, various processing aids and other additives. These elastomers are of special interest in the automotive industry where they can be used as conduits, valves or diaphragms and the like if properly adhesively bound to ancillary metal equipment.

It has however been difficult to bond these surfaces to metals, especially in those instances in which the adhesively bound surfaces are subjected to fuels, oils and other organic solvents.

Accordingly, it is an object of the present invention to provide methods for effectively adhesively bonding metal to rubber surfaces. It is an even more especially preferred object to provide a method for bonding fluorosilicone rubbers to a variety of metallurgies including, stainless steel, mild steel, brass, and aluminum.

Summary of the Invention

These and other objects are met by the instant invention. Effective adherence of rubber, especially fluorosilicone rubbers, to a variety of metal surface has been shown by use of an adhesive treatment comprising (I) an organofunctional silane and (II) a non-organofunctional silane.

The silanes (I) and (II) are partially hydrolyzed by addition thereof to an acidic aqueous or alcoholic medium. Solutions or dispersions of the silanes (I) and (II) are then applied to the requisite rubber or metal surface by dip coating, spraying, roller coating etc. After application of adhesive treatment to the surfaces, the surfaces may be blow dried or heated.

Although emphasis has been placed on effective adhesive bonding of fluorosilicone rubbers to a variety of metal surfaces, the adhesive treatment may also be used in conjunction with other rubber types such as EPDM, fluorocarbon rubber, and vinyl methyl silicone rubber. Tested metals with which the adhesive treatment has demonstrated efficacy include brass, stainless and mild steel and aluminum.

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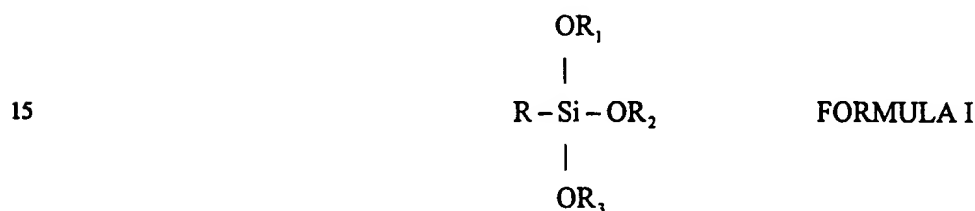
The invention will now be more specifically described in the following detailed description.

Detailed Description of the Preferred Embodiment

5 The adhesive treatment of the invention comprises use of an organofunctional silane (I) and a non-organofunctional silane (II).

I. Organofunctional silane

This is a substituted silane compound having at least one free
10 organofunctional moiety attached to an Si atom wherein the organofunctional moiety is adapted to react with the rubber substrate. More preferably, the organofunctional moiety is attached to one end of the Si atom with the remaining Si valences bonded to groups selected from C₁-C₆ alkoxy or acetoxy. More particularly, suitable organofunctional silane compounds can be represented by the formula



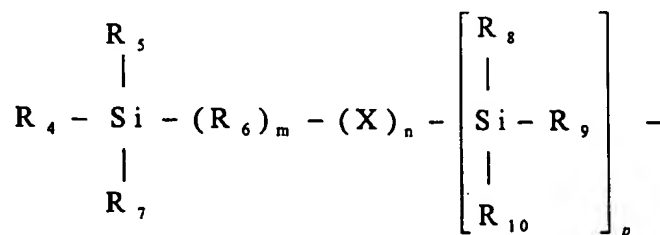
wherein R is chosen from amino, C₁-C₆ alkylamino, vinyl, ureido, ureido substituted C₁-C₆ alkyl, epoxy, epoxy substituted C₁-C₆ alkyl, mercapto, mercapto substituted C₁-C₆ alkyl, cyanato, cyanato substituted C₁-C₆ alkyl, methacrylato, methacrylato substituted C₁-C₆ alkyl, and vinyl benzyl moieties. The most preferred R substituent
20 is vinyl. R₁, R₂, and R₃ are independently selected from C₁-C₆ alkyl and acetyl groups.

Exemplary organofunctional compounds include γ - aminopropyltriethoxysilane (γ-APS); γ- mercaptopropyltrimethoxysilane (γ-MPS); γ-ureidopropyltrialkoxysilanes (γ-UPS); γ-glycidoxypropyltrimethoxysilane (γ-
25 GPS); and a host of vinyl silanes (wherein R is vinyl). Most preferred are vinyltrimethoxysilane, vinyltriethoxysilane and vinyltriacetoxysilane with vinyltrimethoxysilane (VS) most preferred.

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II. Non-Organofunctional Silane

These are substituted silane compounds wherein one or a plurality of the Si valences are bonded to C₁-C₆ alkoxy and/or acetoxy groups. These may be
 5 represented by the formula II



wherein m is 0 or 1; n is 0 or 1; and p is 0 or 1; with R₄ selected from an aliphatic (saturated or unsaturated) group; aromatic group, or C₁-C₆ alkoxy or acetoxy; R₅, R₆,
 10 R₇, R₈, R₉, and R₁₀ may be the same or different and are chosen from C₁-C₆ alkoxy, H, or acetoxy; X, when present, is alkylene, alkenylene, phenylene or amino.

Exemplary non-organofunctional silanes include methyltrimethoxysilane (MS); propyltrimethoxysilane (PS); 1, 2 bis (triethoxysilyl) ethane (BTSE); bis (methyl diethoxysilyl) ethane (BDMSE); 1, 2-bis
 15 (trimethoxysilyl) ethane (TMSE); 1, 6 - bis (trialkoxysilyl) hexanes; 1, 2 - bis - (triethoxysilyl) ethene; and 1, 2 - bis - (trimethoxysilylpropyl) amine. Preferred are BTSE and BDMSE with BTSE most preferred.

The organofunctional silanes (I) and the non-organofunctional silanes (II) are both partially hydrolyzed by addition thereto into an aqueous/alcoholic
 20 solution including preferably a 40/60 vol% mix of ethanol/water. The silanes are added in an amount by volume of 0.5-10% based on the volume of the aqueous/alcoholic solution. Preferably, the silanes are present in an amount by volume of from about 1-5 vol%. Optimal adhesion has been shown when the pH of the solution is adjusted to between about 1-7. Most preferred is a pH of about 4.

25 The hydrolyzation of the silanes I and II is dependent on the pH of the solution. For example, acetic acid, oxalic acid and phosphoric acid may be

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mentioned as exemplary pH adjustment agents. Based on presently available data, it is preferred to use acetic acid as the pH adjustment agent.

Preliminary results indicate that the solution should be an ethanol/water solution with a 40/60 ethanol:water volumetric ratio being presently preferred.

The intended interfacial surfaces of the metal to rubber parts are contacted by the silanes (I) and (II) by dipping, spraying, painting etc. The following procedures were tried and found effective:

(1) blow drying - the metal parts are dipped in the silane solution for at least 30s and then are blown dry by filtered air;

(2) air drying - the metal parts are dipped into the silane solution for at least 30s and are allowed to dry for at least 30min in the air;

(3) prebaking - the metal parts are dipped into the silane solution for at least 30s and then dried in an air circulated oven for 20min at 120°C;

(4) spraying - the silane solution was sprayed on the metal parts and the parts were blown dry by filtered air; and

(5) preheated spraying - the silane solution was sprayed onto the metal parts which were then preheated in an air circulated oven for 20min and then blown dry by filtered air. In those situations in which brass metallurgy is to be adhesively bound to desired rubber, the blow drying and spraying techniques appear optimal.

When brass and fluorosilicone substrates are to be bonded, a mixture of VS and BTSE should be used in a single layer approach. A mixture of 3% VS and 2% BTSE in EtOH/H₂O appears optimal in this situation.

Surprisingly it was found that a two step or two layer coating system appeared optimal for Al, SS and MS metals. That is, a first layer of non-organofunctional silane (II) is applied to the metal surface. Then, the organofunctional silane (I) is applied over the first layer as a second layer. This second layer consisting of the organofunctional silane (I) is placed adjacent the rubber surface for effective bonding. Of course the second layer could be placed

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over the rubber substrate with the metal and rubber surfaces then placed together and pressed to effect bonding.

Although applicants are not to be bound by any particular theory of operation, it is thought that the available organofunctional moiety on the silane effectively cross links with the rubber, probably to diene functions along the rubber macromolecule.

Based upon presently available data, the two step approach is preferred for Al, SS, and MS - rubber adhesion. The first layer solution should be 1% BTSE at pH 4 with the second layer solution being a VS 5% solution at pH 4.

For brass, a single layer mixture of VS and BTSE is presently preferred. Both the VS and BTSE are commercially available from Witco's Organosilicone group in Tarrytown, New York.

Although the present research indicates that the adhesive treatments of the present invention are effective for peroxide cured rubbers, it is thought that the invention shall also function for other curing systems such as nitro, quinone, azo, S, Se, bisphenol, diamine, Pt and Te curing systems.

Additional research has also shown that sandwiches of silicon wafers and siloxane rubber can be joined with the two step process and that these joints can successfully withstand etching with a 50% KOH solution at 80°C.

Examples

In order to assess the efficacy of the silane adhesive treatments of the present invention in bonding metal to rubber surfaces, a series of tests were performed with test specimens as set forth in the ISO 5600 standard test except that the actual dimensions of the parts were slightly modified in order to make the tests more economical.

In accordance with the ISO 5600 procedure, the test piece is composed of two conical ends of a rigid material (or here, metal), joined by a cylinder of rubber. The rigid material comprises a pair of metal insert parts: each containing a conical end and an opposed cylindrical end. The diameter of the

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cylindrical ends is 12.5 mm, while the half angle of the conical vertex is 45°. The two conical ends of the inserts are spaced apart from each other with the cylindrical rubber material provided, at its opposed longitudinal ends, with "V" shaped concavities; each adapted to mate with a conical end of one of the rigid inserts. The insert-rubber-insert combination is aligned so that a space of about 6 mm separates the tip end of one conical insert from the tip end of the other.

The test adhesives are applied along the interfacial surfaces of each of the "V" shaped concavities of the rubber material and the conical ends of the inserts. The so formed test rubber pieces are vulcanized in a suitable transfer mould for 6 minutes at 170°C under a clamp pressure of 60 bar. The test pieces were then postcured for 7h at 200°C.

The alloys used in the studies were as follows:

Tested metal alloys

Metal Code	Metal	Alloy	Pre-treatment
SS	Stainless Steel	X12CrMoS17 (AISI430F)	alkaline
MS	Mild Steel	9SMn36	degreased
AL	Aluminium	AlSiMgl	alkaline
Br	Brass	CuZn39Pb3	acidic

The above Table also shows the metal pre-treatments used in this research. The aluminum and stainless steel parts were cleaned ultrasonically in a Sonotron-solution of 5% in distilled water (pH10) for 10 minutes at 50°C. Sonotron is a commercial alkaline cleaner obtained from Rogier Bosman Chemie B.V. (The Netherlands). Afterwards the samples were rinsed thoroughly with distilled water and immediately dipped in the silane solution. The brass parts were cleaned ultrasonically in a Deoxidine-solution of 5% in distilled water (pH1) for 10 minutes at room temperature. Deoxidine is a commercial acidic cleaner obtained from Mavom B.V. (The Netherlands). This was found to be the best pre-treatment procedure for brass. Afterwards the samples were thoroughly rinsed with distilled water and immediately dipped in the silane solution. Finally the mild steel parts were ultrasonically degreased in a 50/50% mixture of acetone and ethanol, rinsed in ethanol and dipped

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into the silane solution. Cleaning with the commercial aqueous systems caused immediately corrosion of the mild steel parts.

After cleaning, the metal parts were dipped for at least 30s in the silane coupling agent solutions and blown dry by air. In some experiments the metal parts were dipped in a second solution for at least 30s, immediately after drying, and blown dry by air. In other experiments the parts were dried in an oven for 20min at 120°C or just air dried. Further in some cases sodium silicate (10% solution; Fisher Chemicals (USA)) was applied followed by dipping in a silane solution.

Adhesive efficacy was tested by an Instron tensometer at a constant crosshead speed of 2 inch/min. The maximum force [N] for failure of the test parts and the rubber retention [%R] – (100% rubber retention means complete failure of the test parts in the rubber phase) were measured and recorded. Reported results use the average of three tests.

Prior to testing of the bond strength at least 16h conditioning at room temperature was allowed. Three tests parts of every four runs were used for initial tests and six parts for the aging tests. The tests were carried out as described above.

In some cases, the test parts were “aged.” For these studies, test parts were immersed in a mixture of 85% ASTM reference fuel C, a 50/50% blend of toluene and isooctane, and 15% methanol. Addition of 15-25% of methanol is known to cause the highest property loss and volume swell for fluorosilicone parts. The fuel tests were carried out with stainless steel chambers which were filled with the fuel mixture and sealed off with a Viton® O-ring. The chambers were put in an oven for 70h at 60°C. After 70h the stainless steel chambers were taken out off the oven and some test parts were allowed to cool down to reach room temperature, still soaked in the fuel. After this cool down period, the test pieces were taken out of the fuel, dried with a tissue and immediately tested to avoid evaporation of the fuel. Other parts, after the fuel soak, were put in an oven for 24h at 100°C to evaporate the fuel and tested.

30 Results

1.0 Effect of silane coupling agents on bonding strength

Tables 1 and 2 show the effect of various silanes by themselves on the adhesion strength for aluminum and brass. As references the cleaned metal parts (no adhesive layer) and sodium silicate were used.

5

Table 1: Silane coupling agents for bonding of fluorosilicone rubber to aluminum (parts dipped in solution in 40% ethanol/60% water mixture (only MS and PS applied in 80% ethanol/20% water mixture) of 5 vol% at pH4)

Type of silane	Maximum Force [N]	Rubber Retention [%R]
none	40	0
Sodium Silicate	99	0
MS	26	0
VS	295	100
BTSE	308	100
BDMSE	216	65
PS	168	50

10

Table 2: Silane coupling agents for bonding of fluorosilicone rubber to brass (parts dipped in solution of 5 vol% in 40% ethanol/water mixture at pH4)

Type of silane	Maximum Force [N]	Rubber Retention [%R]
none	47	0
Sodium Silicate	55	0
MS	76	0
VS	281	100
BTSE	214	25
BDMSE	230	55

MS = methyltrimethoxysilane

VS = vinyltrimethoxysilane

15 BTSE = 1, 2 bis (triethoxysilyl) ethane

BDMSE = Bis (methyldiethoxysilyl) ethane

PS = n-propyltrimethoxysilane

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From Tables 1 and 2 it is clear that silane coupling agents by themselves are useful for bonding of fluorosilicone rubber to metals.

A sodium silicate-layer does not have any organofunctionality. Therefore during the vulcanization of rubber no bonds can be formed across the silicate-rubber interface. This co-vulcanization did not take place when methyltriethoxysilane was used. Vinyl moieties are known for their reactivity during vulcanization and therefore the adhesion improved radically when vinyltrimethoxysilane was used.

Further it was surprising that BTSE, BDMSE and n-propyltrimethoxysilane, known as non-functional silanes, were able, to a certain extent, to bond fluorosilicone rubber to metals.

2.0 Adhesion using mixed silane coupling agents

The adhesive efficacy of mixtures of VS and BTSE was assessed along with mixtures of PS and MS with VS.

Table 3 shows the results of different mixtures of VS and BTSE on the adhesion of fluorosilicone rubber to brass.

Table 3: Influence of the ratio of VS and BTSE on the adhesion of metals to fluorosilicone with a mixture of VS and BTSE (solution in 40% ethanol/water mixture with pH4; VS and BTSE were added in the given vol%)

Mixture VS+BTSE	Aluminum		Stainless Steel		Mild Steel	
5% + 0% ^a	295 ^b	100 ^c	289	100	305	100
3% + 2%	296	100	286	100	291	100
5% + 1%	303	100	293	85	303	100
5% + 2%	301	100	285	95	307	100
5% + 5%	286	95	291	95	306	100
0% + 5%	308	100	285	100	297	100

^a VS [vol%] + BTSE [vol%]

^b Maximum Force [N]

^c Rubber Retention [%R]

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Table 4: Mixtures of MS and PS with VS (solution in 40% ethanol/water mixture with pH4) for aluminum - FVMQ adhesion

Silane mixture	Initial		Fuel		Dry-Out	
3%VS + 2%PS	282 ^a	100 ^b	114	95	294	95
3%VS + 2%MS	298	100	115	100	302	100

^a Maximum Force [N]

^b Rubber Retention [%R]

5

These results demonstrate that by adding VS, interfacial bonds are formed during the vulcanization of the rubber.

FVMQ = fluorinated, vinyl methyl silicone rubber

10 3.0 Two Step Process

Not always a nice homogeneously layer is obtained when a silane is applied to a substrate. Surface wetting and chemistry can lead to deficiencies in the silane layer and disorientation of the silane at the substrate interface. This phenomena has been demonstrated for γ -aminopropylsilane. The amino group could be oriented towards the substrate or from the substrate depending on the pH.

15

Therefore it could be beneficial to apply first a layer of a silane which shows strong interaction with the substrate forming thus a homogeneous and a dense layer on the substrate followed by applying a silane which adheres very well to the first silane layer and which will be oriented in the right direction. In this way good adhesion can be obtained between two substrates.

20

Bis-(trimethoxysilyl)ethane has twice as many silanol groups as other commonly used silanes. BTSE has six silanol groups when it is completely hydrolyzed and more common silanes have three silanol groups. Therefore BTSE should react readily with the hydroxyl groups on the metal surface forming a homogeneously and dense layer.

25

In these experiments a variety of two layer systems was compared. The performance of BTSE as first layer was compared with BDMSE which has only four silanol groups when it is completely hydrolyzed, and with sodium silicate.

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Concentration and pH were varied. In all cases vinyltrimethoxysilane was applied as second layer at a concentration of 1% or 5% with pH4.

Table 5: Fluorosilicone elastomer bonded to aluminum with a variety of two step processes

Two Step Process	Maximum Force [N]	Rubber Retention [%R]
BTSE (1%) pH4 + VS (5%) pH4	294 ^a	100 ^b
BTSE (1%) pH7 + VS (1%) pH4	231	40
BTSE (1%) pH7 + VS (5%) pH4	276	95
BTSE (5%) pH4 + VS (5%) pH4	282	95
BTSE (5%) pH5 + VS (5%) pH4	294	100
BTSE (5%) pH6 + VS (5%) pH4	294	100
BTSE (5%) pH7 + VS (5%) pH4	280	100
BTSE (5%) pH7 + VS (1%) pH4	279	100
BDMSE (5%) pH4 + VS (5%) pH4	314	100
Silicate (10%) pH11 + VS (5%) pH4	308	100

^a Maximum Force [N]

^b Rubber Retention [%R]

- 10 For aluminum all two step processes gave 100% rubber retention (Table 5) except the two layer system of BTSE (1%) pH7 and VS (1%) pH4.

The results in Table 6 show that for the majority of the two step processes 100% rubber retention can be obtained for stainless steel. Only applying BTSE from a 5% solution with pH7 decreases the adhesion.

15

Table 6: Fluorosilicone elastomer bonded to stainless steel with a variety of two step processes.

Two Step Process	Maximum Force [N]	Rubber Retention [%R]
BTSE (1%) pH4 + VS (5%) pH4	294 ^a	100 ^b
BTSE (1%) pH7 + VS (1%) pH4	294	100
BTSE (1%) pH7 + VS (5%) pH4	288	100
BTSE (5%) pH4 + VS (5%) pH4	291	100
BTSE (5%) pH5 + VS (5%) pH4	284	95
BTSE (5%) pH6 + VS (5%) pH4	291	95
BTSE (5%) pH7 + VS (5%) pH4	216	15
BTSE (5%) pH7 + VS (1%) pH4	162	15
BDMSE (5%) pH4 + VS (5%) pH4	327	100
Silicate (10%) pH11 + VS (5%) pH4	298	80

^a Maximum Force [N]^b Rubber Retention [%R]

5 Table 7: Fluorosilicone elastomer bonded to mild steel with a variety of two step processes

Two Step Process	Maximum Force [N]	Rubber Retention [%R]
BTSE (1%) pH4 + VS (5%) pH4	303 ^a	100 ^b
BTSE (1%) pH7 + VS (1%) pH4	291	75
BTSE (1%) pH7 + VS (5%) pH4	295	100
BTSE (5%) pH4 + VS (5%) pH4	283	95
BTSE (5%) pH5 + VS (5%) pH4	296	100
BTSE (5%) pH6 + VS (5%) pH4	271	55
BTSE (5%) pH7 + VS (5%) pH4	282	75
BTSE (5%) pH7 + VS (1%) pH4	228	45
BDMSE (5%) pH4 + VS (5%) pH4	254	25
Silicate (10%) pH11 + VS (5%) pH4	232	15

^a Maximum Force [N]^b Rubber Retention [%R]

10

For brass 100% rubber retention was only obtained with BTSE (5%) pH4 and VS (5%) pH4 (Table 8). Brass surfaces look to be very sensitive to applying conditions and the solutions have to be fine tuned.

Table 8: Fluorosilicone elastomer bonded to brass with a variety of two step processes

Two Step Process	Maximum Force [N]	Rubber Retention [%R]
BTSE (1%) pH4 + VS (5%) pH4	234 ^a	30 ^b
BTSE (1%) pH7 + VS (1%) pH4	266	65
BTSE (1%) pH7 + VS (5%) pH4	241	40
BTSE (5%) pH4 + VS (5%) pH4	287	100
BTSE (5%) pH5 + VS (5%) pH4	247	65
BTSE (5%) pH6 + VS (5%) pH4	119	20
BTSE (5%) pH7 + VS (5%) pH4	262	70
BTSE (5%) pH7 + VS (1%) pH4	197	20
BDMSE (5%) pH4 + VS (5%) pH4	242	15
Silicate (10%) pH11 + VS (5%) pH4	211	15

5 ^a Maximum Force [N]

^b Rubber Retention [%R]

4.0 Aging Tests

It is important that the adhesive agents should endure a 70h test in a mixture of 85% ASTM reference fuel C, a 50/50% blend of toluene and isooctane, and 15% methanol. Not only the rubber will be affected by the fuel mixture but also the silane coupling agent layer and the interfaces. The stress at those interfaces and in the silane layer will be increased during swelling of the elastomer. The resistance of the layer against the fuel will be determined by the layer thickness, the (crosslink) density of the layer, the interactions between the silane and the metal substrate on one side and the interaction of the silane with the elastomer on the other side.

A possible loss in adhesion will maybe not be observed after immersion of the test parts in the fuel. The rubber is then completely swollen and the strength of the rubber is decreased. However, after dry out and evaporation of the solvents the rubber will regain its strength back and a possible loss in adhesion will be observed. In tests involving aluminum to FVMQ, after fuel swell and after dry out 100% rubber retention is obtained. The adhesion is not affected by the aging test.

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The rubber strength is affected as can be seen from the decrease (two thirds) of the maximum force for failure after immersion in the fuel. After dry-out, the rubber regained its strength back and the maximum force is close to the initial force for failure.

5 100% rubber retention is obtained initially and after fuel swell for adhesion of brass to FVMQ using a two step process of BTSE (5% at pH4) and VS (5% at pH4). However, after dry-out a substantial decreased is observed in rubber retention suggesting that the adhesion is affected by the fuel immersion and the dry-out process.

10 In Tables 9-12 the results are given for the adhesion of the four tested metals to FVMQ using a variety of silane treatments. With aluminum the best results were obtained and for almost all silane treatments 100% rubber retention was obtained after aging.

Table 9: Adhesion properties after aging test for aluminum bonded to FVMQ

15

Type of Silane Layer	Initial		Fuel Test		Dry-Out Test	
VS (1%) pH4	277 ^a	100 ^b	99	100	289	95
VS (5%) pH4	295	100	96	100	284	90
BTSE (5%) pH4	308	100	92	100	268	100
Mixture VS+BTSE (3%+2%) pH4	296	100	99	100	285	100
BTSE (1%) pH4 + VS (5%) pH4	294	100	99	100	275	100
BTSE (1%) pH7 + VS (1%) pH4	231	40	96	100	267	70
BTSE (1%) pH7 + VS (5%) pH4	276	95	98	100	289	100
BTSE (5%) pH4 + VS (5%) pH4	282	95	94	100	270	100
BTSE (5%) pH7 + VS (1%) pH4	279	100	99	100	291	100
BTSE (5%) pH7 + VS (5%) pH4	280	100	96	100	287	85
BDMSE (5%) pH4 + VS (5%) pH4	314	100	99	100	282	100
Silicate (10%) pH11 + VS (5%) pH4	308	100	98	100	279	90

^a Maximum Force [N]

^b Rubber Retention [%R]

Initial results were for stainless steel also good for a variety of silane
 20 treatments. However, after fuel immersion and dry-out adhesion dropped for a

number of treatments suggesting that the adhesion with these silane treatments was affected by the fuel aging. For three two step processes 100% rubber retention was obtained:

- BTSE (1%) pH4 + VS (5%) pH4
- 5 ■ BTSE (1%) pH7 + VS (5%) pH4
- BDMSE (5%) pH4 + VS (5%) pH4

Table 10: Adhesion properties after aging test for stainless steel bonded to FVMQ

Type of Silane Layer	Initial		Fuel Test		Dry-Out Test	
VS (1%) pH4	285 ^a	95 ^b	69	25	154	0
VS (5%) pH4	289	100	102	100	241	75
BTSE (5%) pH4	285	100	68	40	199	5
Mixture VS+BTSE (3%+2%) pH4	286	100	100	75	237	75
BTSE (1%) pH4 + VS (5%) pH4	294	100	98	100	285	100
BTSE (1%) pH7 + VS (1%) pH4	294	100	101	100	240	60
BTSE (1%) pH7 + VS (5%) pH4	288	100	103	100	271	95
BTSE (5%) pH4 + VS (5%) pH4	291	100	91	80	223	45
BTSE (5%) pH7 + VS (1%) pH4	162	15	52	75	125	0
BTSE (5%) pH7 + VS (5%) pH4	216	15	99	75	186	20
BDMSE (5%) pH4 + VS (5%) pH4	327	100	100	100	277	100
Silicate (10%) pH11 + VS (5%) pH4	298	80	96	100	270	80

10 ^a Maximum Force [N]

^b Rubber Retention [%R]

In case of mild steel applying first a silane of BTSE from a 1% solution followed by a vinylsilane layer from a 5% solution resulted in 100% rubber retention. However, with the one step processes of only vinylsilane and a mixture of VS and BTSE also good results were obtained.

Table 11: Adhesion properties after aging test for mild steel bonded to FVMQ

Type of Silane Layer	Initial		Fuel Test		Dry-Out Test	
VS (1%) pH4	237 ^a	0 ^b	77	35	168	0
VS (5%) pH4	305	100	98	100	272	100
BTSE (5%) pH4	297	100	96	100	219	10
Mixture VS+BTSE (3%+2%) pH4	291	100	97	100	274	85
BTSE (1%) pH4 + VS (5%) pH4	303	100	98	100	285	100
BTSE (1%) pH7 + VS (1%) pH4	291	75	96	100	238	40
BTSE (1%) pH7 + VS (5%) pH4	295	100	98	100	274	90
BTSE (5%) pH4 + VS (5%) pH4	283	95	96	65	249	65
BTSE (5%) pH7 + VS (1%) pH4	228	45	92	75	210	5
BTSE (5%) pH7 + VS (5%) pH4	282	75	100	100	228	30
BDMSE (5%) pH4 + VS (5%) pH4	254	25	93	65	253	35
Silicate (10%) pH11 + VS (5%) pH4	232	15	99	75	210	15

^a Maximum Force [N]^b Rubber Retention [%R]

- 5 Aluminum is very easy to bond to FVMQ using silanes. Brass is most difficult to bond to FVMQ. Best results were obtained for a mixture of 3% VS and 2% BTSE. Similar results were obtained with these solutions. With only vinylsilane also reasonable adhesion was obtained.

10 Table 12: Adhesion properties after aging test for brass bonded to FVMQ

Type of Silane Layer	Initial		Fuel Test		Dry-Out Test	
VS (1%) pH4	283 ^a	90 ^b	94	100	222	5
VS (5%) pH4	281	100	96	100	272	65
BTSE (5%) pH4	214	25	89	90	200	35
Mixture VS+BTSE (3%+2%) pH4	308	95	90	100	269	90
BTSE (1%) pH4 + VS (5%) pH4	234	30	99	100	199	20
BTSE (1%) pH7 + VS (1%) pH4	266	65	93	100	207	15
BTSE (1%) pH7 + VS (5%) pH4	241	40	92	100	227	25
BTSE (5%) pH4 + VS (5%) pH4	287	100	89	100	197	40
BTSE (5%) pH7 + VS (1%) pH4	197	20	78	75	115	0
BTSE (5%) pH7 + VS (5%) pH4	262	70	88	95	197	15

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BDMSE (5%) pH4 + VS (5%) pH4	242	15	84	65	230	15
Silicate (10%) pH11 + VS (5%) pH4	211	15	85	55	193	10

^a Maximum Force [N]^b Rubber Retention [%R]^c Only the fuel test results of the 3:2 mixture is listed in this table.

5 Generally the following can be concluded from the aging test results:

- Aluminum is easy to bond and the formed bond is not sensitive to a fuel environment.
 - Brass is more difficult to bond and best results were obtained with a mixture of VS and BTSE
- 10 ■ For stainless Steel and mild Steel with one specific two step process (BTSE-1% (pH4) and VS-5% (pH4)) 100% rubber retention was obtained.
- If one has to select a general silane treatment for aluminum, stainless steel and mild steel the two step process of BTSE-1% (pH4) and VS-5% (pH4) would be the best process.
- 15 ■ Immersion in fuel decreases the maximum force for failure at 100% rubber retention with two third.
- After dry-out the maximum force for failure is comparable with the initially measured force. Some silane layers in combination with a type of metal are very sensitive to this aging test. This is probably due to differences in silane layer
- 20 thickness, the (crosslink) density of the layer, the interactions between the silane and the metal substrate on one side and the interaction of the silane with the elastomer on the other side. On aluminum a nice homogeneous and dense layer with good interactions with the metal surface can be easily obtained.

25 5.0 Adhesive tests with other elastomers

Several silane solutions were also evaluated on the ability to adhere other elastomer types to stainless steel and aluminum:

- EPDM: Ethylene Propylene Diene Rubber
- VMQ: Vinyl Methyl Silicone Rubber

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■ FKM: Fluorocarbon Rubber

Molding of the rubber-metal test parts

The rubber-metal test parts were prepared by hot transfer molding at a vulcanization
5 temperature of 170°C for the silicone compounds. The EPDM and FKM compounds
were molded at a temperature of 185°C. For all compounds the vulcanization time
was set at 6min and the ram pressure was 60bars. After molding the test pieces were
post cured for variable amounts of time depending on the elastomer type to stabilize
final properties and to remove volatile peroxide decomposition products:

- 10 ■ Silicone test parts 4h @ 200°C
■ Fluorocarbon test parts 7h @ 230°C
■ EPDM test parts no post cure

Aging tests Fluorocarbon test parts

- 15 The same procedure was followed as described for the fluorosilicone parts. Only the
parts were soaked in Fuel C without addition of methanol and the aging temperature
was 70°C instead of 60°C.

Durability tests EPDM test parts

- 20 Some EPDM test parts were immersed in a 50/50% ethylene glycol and distilled
water mixture. This system was heated to 135°C under an over-pressure of 2.5 bar in
an autoclave. The test pieces were subjected to this environment for 22h. The parts
were cooled to room temperature and tested as described above. Other test parts
were subjected to either a solution of 50mM citric acid (pH3) or a 3%-NaOH
25 solution for 22h at refluxing temperature.

Durability tests silicone test parts

The same procedure was followed as described for the EPDM parts. Only the parts
were immersed in distilled water.

Results and Discussion

Table 13 shows the results when EPDM is adhered to stainless steel and aluminum using silane coupling agents. The performance of only VS, a mixture of VS and BTSE and the two step process using first a layer of BTSE either applied from a 1% or a 5% solution were compared before and after an autoclave test. For stainless steel all the tested silane systems were giving about 100% rubber retention before and after autoclave testing. For aluminum the two step processes showed initially 100% rubber retention but after autoclave there is hardly any difference between the systems (about 70% rubber retention). The aluminum looked affected by the water/glycol environment. This environment is slightly acidic (pH5) and the aluminum parts are possibly affected by this environment.

Table 13: Adhesion of EPDM to stainless steel and aluminum using silane coupling agents

Metal	VS (5%)		BTSE (1%) + VS (5%)		BTSE (5%) + VS (5%)		Mixture VS + BTSE (3% + 2%)	
Stainless Steel (before autoclave)	560 ^a	100 ^b	569	100	576	100	556	100
Stainless Steel (after autoclave)	523	95	538	100	544	100	530	90
Aluminum (before autoclave)	538	70	554	100	572	100	503	75
Aluminum (after autoclave)	494	70	493	75	448	60	506	75

^a Maximum Force [N]

^b Rubber Retention [%R]

Table 14 gives results of durability tests in other environments.

Especially the results in the 3%-NaOH solution are remarkable because this is a very severe environment. In the citric acid environment both the rubber and the stainless steel parts seemed attacked but the adhesion was unaffected (citric acid solution was colored black with the EPDM and the metal parts looked corroded).

Table 14: Durability of EPDM to stainless steel joints using a two step process
(BTSE-1% (pH4) and VS-5% (pH4))

Test environment ^a	Maximum Force for failure [N]	Rubber retention [%R]
50 mM Citric acid (pH3)	508	100
3%-NaOH	505	80

^a Tested for 22h at refluxing temperature \pm (100°C)

5 Two types of FKM compounds were tested. These compounds differ significantly in rheologic properties (see Table 15). With compound FKM-1 problems arose with processing of the compound. Therefore mold filling was not optimal and adhesion was negatively influenced. Only 20% rubber retention was obtained.

10

Table 15: Adhesion of FKM to stainless steel using silane coupling agents

Type of FKM	VS (5%)		BTSE (1%) + VS (5%)		Mixture VS+BTSE (3% + 2%)	
FKM-1 (before fuel)	340 ^a	20 ^b	332	25	396	30
FKM-2 (before fuel)	360	100	286	100		
FKM-2 (after fuel)	246	90	307	95		
FKM-2 (after dry-out)	244	100	310	95		

^a Maximum Force [N]

^b Rubber Retention [%R]

15

Compound FKM-2 processed very well and good results were obtained with VS and the two layer system. Even after fuel soak and dry out 100% rubber retention was obtained.

20 Table 16: Adhesion of VMQ to stainless steel using silane coupling agents

Type of VMQ	VS (5%)		BTSE (1%) + VS (5%)		Mixture VS+BTSE (3% + 2%)	
VMQ-1 (before autoclave)	179 ^a	100 ^b	178	100	182	100
VMQ-2 (before autoclave)	248	100	239	100		
VMQ-2 (after autoclave)	217	100	218	100		

^a Maximum Force [N]

^b Rubber Retention [%R]

Table 16 shows the results for the siloxane compounds. In case of VMQ-1 failure occurs for 100% in the bulk of the rubber. In case of VMQ-2 failure occurs not in the bulk of the rubber but in a layer very close to the silane layer. SEM photographs show the failure pattern for VMQ-2. It is clear that failure has occurred in the rubber phase. Closer observations of the failure surface showed only a few minor cracks in the rubber layer. EDX-analysis learned that the metal surface could be seen in these cracks but that the metal was covered with the silane coupling agent layer and probably also siloxane rubber. On basis of the SEM-analysis it was determined that failure took place for 100% in the rubber phase.

6.0 Replacement of vinyltrimethoxysilane by vinyltriethoxysilane

One disadvantage of vinyltrimethoxysilane is that in contact with water, methanol can be formed. When vinyltriethoxysilane would be used this problem would be solved. Table 17 shows the results of vinyltriethoxysilane. This silane needs more hydrolysis time and in the presolution about 60% ethanol is needed to solve the silane well in water. After hydrolysis the presolution can be adjusted to the desired concentration of silane and ethanol.

Table 17: Adhesion of FVMQ to stainless steel and aluminum using vinyltriethoxysilane and BTSE (pH4)

One or two step	metal	Initial		Fuel		Dry-Out	
VS-ethoxy 5%	stainless steel	261	75				
BTSE-1% + VS-ethoxy	stainless steel	241	50	106	85	221	45
BTSE-1% + VS-ethoxy	aluminum	301	95	114	100	288	95

^a Maximum Force [N]

^b Rubber Retention [%R]

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For aluminum 100% rubber retention is obtained with the two step process of vinyltriethoxysilane and BTSE, even after aging. With stainless the results are worse and only 45% rubber retention is obtained after aging. Maybe hydrolysis time and presolution composition have to be reconsidered (to complete hydrolysisation).

Preliminary data also suggests that silicon wafers and siloxane rubber can be bonded with the two step process [BTSE - 1% (pH 4) and VS - 5% (pH 4)] and that these joints can successfully withstand etching with a 50% - KOH solution at 80°C. The adhesion of VMQ and FVMQ to silicon wafers has been preliminarily tested. Two types of silicon wafers were tested: 1) a silicon wafer with a silicon oxide surface and 2) a silicon wafer with a nitride coating. Wetting of the silanes on the nitride coating was poor. Adhesion of both wafers to VMQ and FVMQ using the two step process of BTSE - 1% (pH 4) and VS - 5% (pH 4) looked satisfactory. The adhesion also looked good after etching of the silicon with a 50% KOH solution at 80°C (the adhesion interface and the elastomer are exposed to this environment).

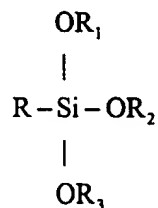
While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.

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1. Method of adhering a metal substrate to a rubber substrate comprising contacting one of said substrates with an effective adhesive amount of an adhesive treatment comprising an organofunctional silane (I) and a non-organofunctional silane (II); said (I) and (II) being at least partially hydrolyzed, and placing said
5 substrates together with said adhesive treatment interposed therebetween to effect said adhering.

2. Method as recited in claim 1 wherein said organofunctional silane (I) includes at least one free organofunctional moiety attached to an Si atom, said organofunctional moiety adapted to react with said rubber substrate.

3. Method as recited in claim 2 wherein said organofunctional silane (I) has the formula



wherein R is a member selected from the group consisting of amino, C₁-C₆
5 alkylamino, vinyl, ureido, ureido substituted C₁-C₆ alkyl, epoxy, epoxy substituted C₁-C₆ alkyl, mercapto, mercapto substituted C₁-C₆ alkyl, cyanato, cyanato substituted C₁-C₆ alkyl, methacrylato, methacrylato substituted C₁-C₆ alkyl, and vinyl benzyl moieties; and R₁, R₂, and R₃ are the same or different and are selected from C₁-C₆ alkyl and acetyl groups.

4. Method as recited in claim 3 wherein R is vinyl.

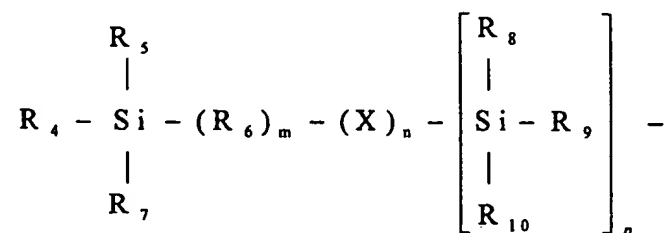
5. Method as recited in claim 4 wherein R₁, R₂, and R₃ are each methyl.

6. Method as recited in claim 4 wherein R₁, R₂, and R₃ are each ethyl.

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7. Method as recited in claim 1 wherein said non-organofunctional silane (II) comprises an Si compound wherein one or a plurality of the Si valences are bonded to C₁-C₆ alkoxy or acetoxy groups.

8. Method as recited in claim 1 wherein said non-organofunctional silane (II) is represented by the formula



wherein m is 0 or 1; n is 0 or 1; and p is 0 or 1; with R₄ selected from an aliphatic (saturated or unsaturated) group; aromatic group, or C₁-C₆ alkoxy; R₅, R₆, R₇, R₈, R₉, and R₁₀, may be the same or different and are chosen from C₁-C₆ alkoxy, H, or acetoxy; X is alkylene, alkenylene, phenylene or amino.

9. Method as recited in claim 8 wherein said non-organofunctional silane is a member selected from the group consisting of methyltrimethoxysilane (MS); propyltrimethoxysilane (PS); 1, 2 bis (triethoxysilyl) ethane (BTSE); bis (methyl diethoxysilyl) ethane (BDMSE); 1, 2-bis (trimethoxysilyl) ethane (TMSE); 1,6-bis (trialkoxysilyl) hexanes and 1, 2-bis(trimethoxysilylpropyl) amine.

10. Method as recited in claim 9 wherein said non-organofunctional silane is BTSE.

11. Method as recited in claim 9 wherein said non-organofunctional silane is BDMSE.

12. Method as recited in claim 1 wherein said contacting comprises dipping one of said substrates in a solution containing said adhesive treatment.

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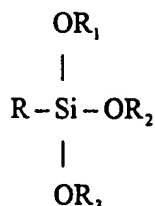
13. Method as recited in claim 12 wherein said adhesive treatment is present in solution at a pH of about 1-7.
14. Method as recited in claim 13 wherein said pH is about 4.
15. Method as recited in claim 12 wherein said adhesive treatment is present in said solution in an amount by volume of about 0.5 - 10%.
16. Method as recited in claim 1 wherein said organofunctional silane (I) is a vinylsilane selected from the group consisting of vinyltrimethoxysilane, vinyltriethoxysilane and vinyltriacetoxysilane.
17. Method as recited in claim 16 wherein said non-organofunctional silane (II) is selected from the group consisting of 1, 2 bis (triethoxysilyl) ethane (BTSE) and bis (methyl diethoxysilyl) ethane (BDMSE).
18. Method as recited in claim 16 wherein said organofunctional silane (I) is vinyltrimethoxysilane (VS) and said non-organofunctional silane (II) is (BTSE).
19. Method as recited in claim 16 wherein said contacting comprises coating said metal substrate with said non-organofunctional silane (II) and then providing a coating of said organofunctional silane (I) over said non-organofunctional silane (II) coating and wherein said step of placing comprises
5 placing said rubber substrate along said coating formed by said organofunctional silane (I) so that said organofunctional silane can bond thereto.
20. Method as recited in claim 19 wherein said non-organofunctional silane (II) is BTSE and wherein said organofunctional silane (I) is vinyltrimethoxysilane (VS).

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21. Method of adhering a metal substrate to a fluorosilicone rubber substrate comprising contacting one of said substrates with an effective adhesive amount of an adhesive treatment comprising an organofunctional silane (I) and a non-organofunctional silane (II) and mixtures of (I) and (II); said adhesive compound
 5 being at least partially hydrolyzed, and placing said substrates together with said adhesive treatment interposed therebetween to effect said adhering.

22. Method as recited in claim 21 wherein said organofunctional silane (I) includes at least one free organofunctional moiety attached to an Si atom, said organofunctional moiety adapted to react with said rubber substrate.

23. Method as recited in claim 22 wherein said organofunctional silane (I) has the formula



wherein R is a member selected from the group consisting of amino, C₁-C₆
 5 alkylamino, vinyl, ureido, ureido substituted C₁-C₆ alkyl, epoxy, epoxy substituted C₁-C₆ alkyl, mercapto, mercapto substituted C₁-C₆ alkyl, cyanato, cyanato substituted C₁-C₆ alkyl, methacrylato, methacrylato substituted C₁-C₆ alkyl, and vinyl benzyl moieties; and R₁, R₂, and R₃ are the same or different and are selected from C₁-C₆ alkyl and acetyl groups.

24. Method as recited in claim 23 wherein R is vinyl.

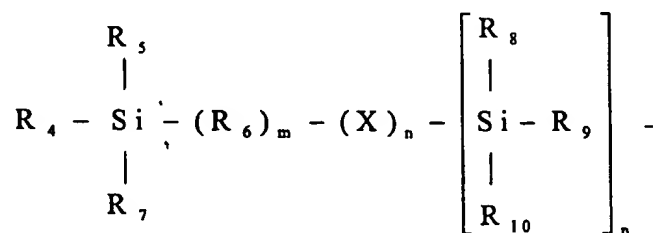
25. Method as recited in claim 24 wherein R₁, R₂, and R₃ are each methyl.

26. Method as recited in claim 24 wherein R₁, R₂, and R₃ are each ethyl.

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27. Method as recited in claim 21 wherein said non-organofunctional silane (II) comprises an Si compound wherein one or a plurality of the Si valences are bonded to C₁-C₆ alkoxy or acetoxy groups.

28. Method as recited in claim 21 wherein said non-organofunctional silane (II) is represented by the formula



wherein m is 0 or 1; n is 0 or 1; and p is 0 or 1; with R₄ selected from an aliphatic
 5 (saturated or unsaturated) group; aromatic group, or C₁-C₆ alkoxy; R₅, R₆, R₇, R₈, R₉,
 and R₁₀ may be the same or different and are chosen from C₁-C₆ alkoxy, H, or
 acetoxy; X is alkylene, alkenylene, phenylene or amino.

29. Method as recited in claim 28 wherein said non-organofunctional
 silane is a member selected from the group consisting of methyl trimethoxysilane
 (MS); propyltrimethoxysilane (PS); 1, 2 bis (triethoxysilyl) ethane (BTSE); bis
 (methyl diethoxysilyl) ethane (BDMSE); 1, 2-bis (trimethoxysilyl) ethane (TMSE);
 5 1, 6 - bis (trialkoxysilyl) hexanes and 1, 2 - bis (trimethoxysilylpropyl) amine.

30. Method as recited in claim 29 wherein said non-organofunctional
 silane is BTSE.

31. Method as recited in claim 29 wherein said non-organofunctional
 silane is BDMSE.

32. Method as recited in claim 21 wherein said contacting comprises
 dipping one of said substrates in a solution containing said adhesive treatment.

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33. Method as recited in claim 32 wherein said adhesive treatment is present in solution at a pH of about 1-7.

34. Method as recited in claim 33 wherein said pH is about 4.

35. Method as recited in claim 32 wherein said adhesive treatment is present in said solution in an amount by volume of about 0.5 - 10%.

36. Method as recited in claim 21 wherein said organofunctional silane (I) is a vinylsilane selected from the group consisting of vinyltrimethoxysilane, vinyltriethoxysilane and vinyltriacetoxysilane.

37. Method as recited in claim 36 wherein said non-organofunctional silane (II) is selected from the group consisting of 1, 2 bis (triethoxysilyl) ethane (BTSE) and bis (methyl diethoxysilyl) ethane (BDMSE).

38. Method as recited in claim 36 wherein said organofunctional silane (I) is vinyltrimethoxysilane (VS) and said non-organofunctional silane (II) is (BTSE).

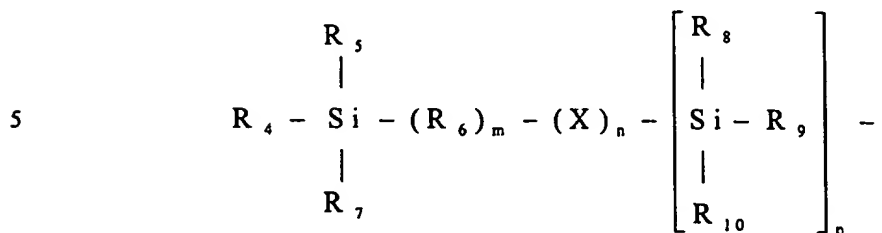
39. Method as recited in claim 36 wherein said contacting comprises coating said metal substrate with said non-organofunctional silane (II) and then providing a coating of said organofunctional silane (I) over said non-organofunctional silane (II) coating and wherein said step of placing comprises
5 placing said rubber substrate along said coating formed by said organofunctional silane (I) so that said organofunctional silane can bond thereto.

40. Method as recited in claim 39 wherein said non-organofunctional silane (II) is BTSE and wherein said organofunctional silane (I) is vinyltrimethoxysilane (VS).

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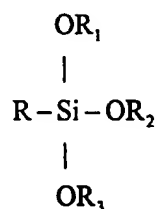
41. A method for adhesively bonding a metal surface to a rubber surface comprising

1) forming a first layer of a non-organofunctional silane on said metal surface, said non-organofunctional silane having the formula



wherein m is 0 or 1; n is 0 or 1; and p is 0 or 1; with R₄ selected from an aliphatic (saturated or unsaturated) group; aromatic group, or C₁-C₆ alkoxy; R₅, R₆, R₇, R₈, R₉, and R₁₀ may be the same or different and are chosen from C₁-C₆ alkoxy, H, or acetoxy; X is alkylene, alkenylene, phenylene or amino; said non-organofunctional
10 silane being at least partially hydrolyzed;

2) providing a second layer of an organofunctional silane having the formula



wherein R is a member selected from the group consisting of amino, C₁-C₆ alkylamino, vinyl, ureido, ureido substituted C₁-C₆ alkyl, epoxy, epoxy substituted C₁-C₆ alkyl, mercapto, mercapto substituted C₁-C₆ alkyl, cyanato, cyanato substituted C₁-C₆ alkyl, methacrylato, methacrylato substituted C₁-C₆ alkyl, and vinyl benzyl moieties, and R₁, R₂, and R₃ are independently selected from C₁-C₆ alkyl and acetoxy groups; said organofunctional silane being at least partially hydrolyzed;

20 3) positioning said second layer between said first layer and said rubber surface and placing said substrates together with said first and second layers interposed between said metal surface and said rubber surface to adhesively bond them together.

42. A method as recited in claim 41 wherein said rubber surface is fluorosilicone rubber, said non-organofunctional silane being selected from the group consisting of 1, 2 bis (triethoxysilyl) ethane (BTSE) and bis (methyl diethoxysilyl) ethane (BDMSE) and wherein said organofunctional silane is a vinyltrialkoxysilane.

43. A method as recited in claim 42 wherein said metal surface is chosen from the group consisting of stainless steel, mild steel, and aluminum surfaces.

44. A method as recited in claim 43 wherein said non-organofunctional silane is BTSE and wherein said vinyltrialkoxysilane is vinyltrimethoxysilane.

45. A method as recited in claim 44 wherein said BTSE is present in an aqueous/alcoholic solution maintained at a pH of about 1-7; said BTSE solution being applied to said metal surface to form said first layer.

46. A method as recited in claim 45 wherein said vinyltrimethoxysilane solution is applied between said first layer and said rubber surface.

47. A method as recited in claim 41 further comprising drying said first and second layers prior to placing said substrates together.

48. A method as recited in claim 46 wherein said BTSE solution has a pH of about 4 and wherein said vinyltrimethoxysilane solution has a pH of about 4.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US98/22576

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C09J 5/04 US CL : 156/326, 314 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 106/287.14, 287.15, 287.16; 156/314, 326; 428/420 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP, 53-232, A (TORAY SILCONE KK) 05 January 1978 (01-05-78), see abstract.	1-2
X --- Y	US, 4,179,537, A (RYKOWSKI) 18 December 1979 (18-12-79), see abstract, column 1, lines 5-22 and 60-68; column 2, lines 1-19; column 3, lines 5-21 and 44-68; column 4, lines 1-23 and 63-68; column 5, lines 7-9.	1-12, 15- 20, 41, 47 ----- 21-32, 35- 40, 42-44
Y	US 4,618,389, A (AGODOA) 21 October 1986 (21-10-86), see abstract, column 1, lines 8-12; column 3, lines 26-44; column 4, lines 4-20.	13-14, 33- 34, 45- 46, 48
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: *A* document defining the general state of the art which is not considered to be of particular relevance *E* earlier document published on or after the international filing date *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) *O* document referring to an oral disclosure, use, exhibition or other means *P* document published prior to the international filing date but later than the priority date claimed *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art *Z* document member of the same patent family		
Date of the actual completion of the international search 11 DECEMBER 1998		Date of mailing of the international search report 25 JAN 1999
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer J.J. GALLAGHER <i>[Signature]</i> Telephone No. (703) 308-0651

INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,363,994, A (ANGELINE) 15 November 1994 (15-11-94) see abstract, column 1, lines 6-13; column 2, lines 4-64; column 4, lines 3-6; column 5, lines 3-37 and 57-68; column 6, lines 1-4 and 22-28.	13-14, 33 - 34, 45-46, 48
Y	US 4,681,636, A (SAITO et al) 21 July 1987 (21-07-87), see abstract, column 1, lines 7-11; column 2, line 4-28 and 47-59; column 3, lines 24-55; column 4, lines 39-61.	21-32, 35- 40, 42-44
Y	US 4,534,815, A (HAMADA et al) 13 August 1985 (13-08-85), see abstract, column 1, lines 12-23; column 2, lines 19-68, column 3, lines 1-14; column 4, lines 5-25.	21-32, 35- 40, 42-44